SILICON DEEP DIVE: SILICON FUNCTIONALIZATION

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Argonne National Laboratory

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2020 DOE VTO Annual Merit Review

Project ID # BAT440

This presentation does not contain any proprietary, confidential, or otherwise restricted information

OVERVIEW

Timeline

- Start: October 1, 2015
  - Reset: October 1, 2017
- End: September 30, 2020
- Percent Complete: 89%

Budget

- Total project funding:
  - FY20 - $3,000,000
- Presentations:

BAT388, BAT439, BAT440

Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and U.S. DRIVE goals
  - Cost, Performance, and Safety

Partners

- Argonne National Laboratory
- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory
- Pacific Northwest National Laboratory
- *Academic Partners*: UMass-Boston, Western Michigan University, University of Illinois-Chicago, University of Tennessee, University of California

RELEVANCE

The **Silicon Deep Dive Next-Generation Anode Program** addresses the cost and performance issues preventing the inclusion of silicon into a commercial lithium-ion cell

- Elemental silicon can theoretically store >3500 mAh/g.
- Battery Performance and Cost (BatPaC) Model indicates a silicon based anode coupled with a high capacity cathode lithium-ion technology presents a pathway to less than $125/kWh$_{use}$.
- Silicon-based electrodes require different components than graphitic carbon anodes due to surface chemistry, SEI stability, conductivity stability, and volume expansion.
- Stabilizing the surface of silicon is a pathway towards limiting detrimental side reactions with electrolyte on cycling.

Objective: Stabilization of silicon-based materials an electrodes leading to successful incorporation into electrochemical cells

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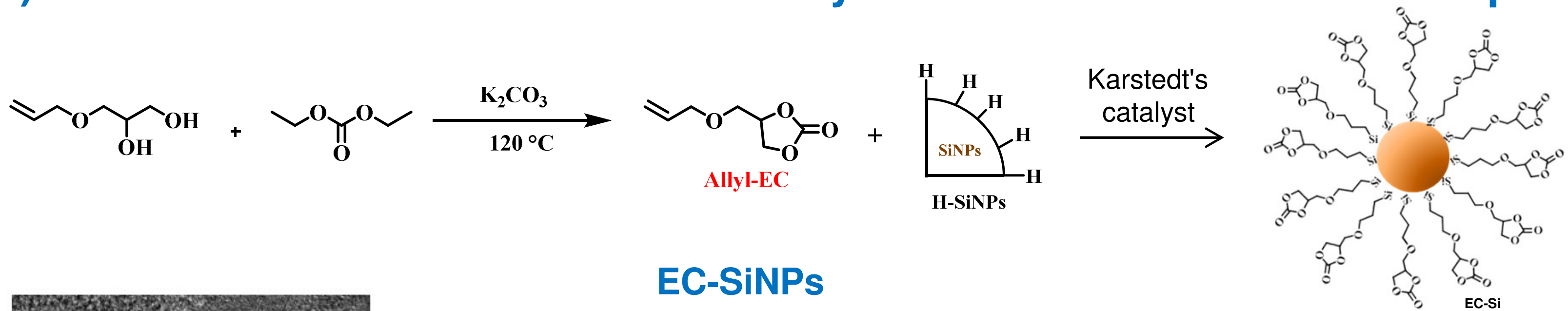
APPROACH

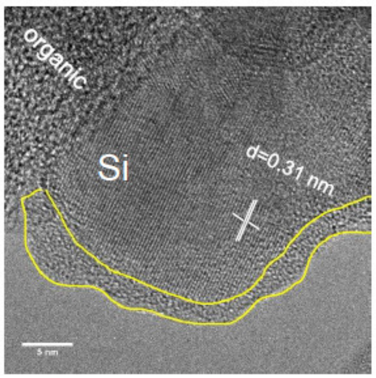
- A multilevel technical approach was employed to tackle the interfacial instability associated with the Si anode in this Deep-Dive program:
  - Si nanoparticle (SiNPs) surface functionalization *via* hydrosilylation chemistry to suppress the chemical/electrochemical reactivity at the surface of Si and Li_xSi.
  - Development of new electrolytes designed to modify and stabilize the Si/electrolyte interface.

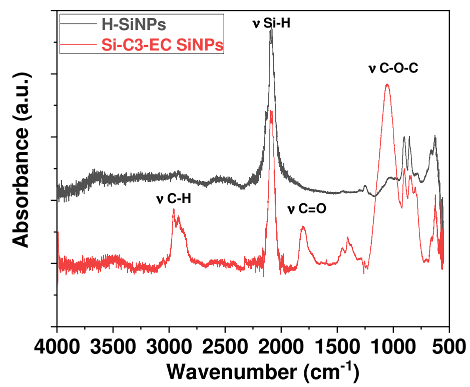
- National Laboratory-based Resources
  - Battery Abuse Testing Laboratory (BATLab), Battery Manufacturing Facility (BMF), Cell Analysis, Modeling, and Prototyping (CAMP), Materials Engineering Research Facility (MERF), Post-Test Facility (PTF)

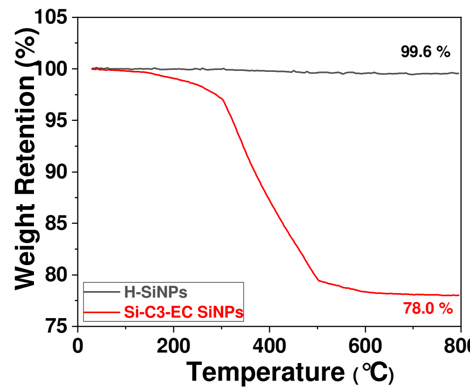
(1) SiNPs Surface Functionalization: Cyclic Carbonate Surface Group

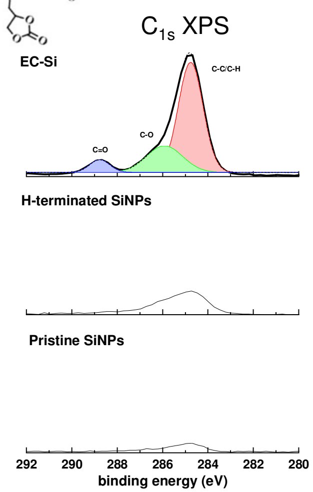


EC-SiNPs





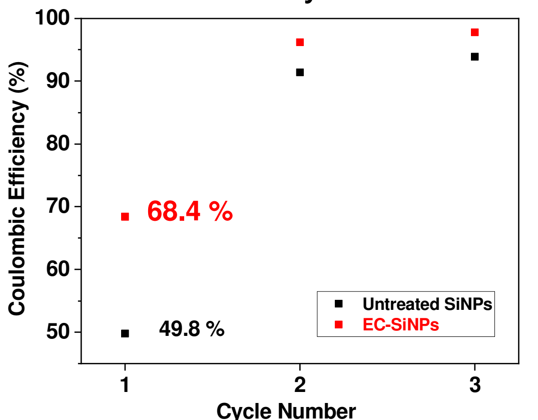


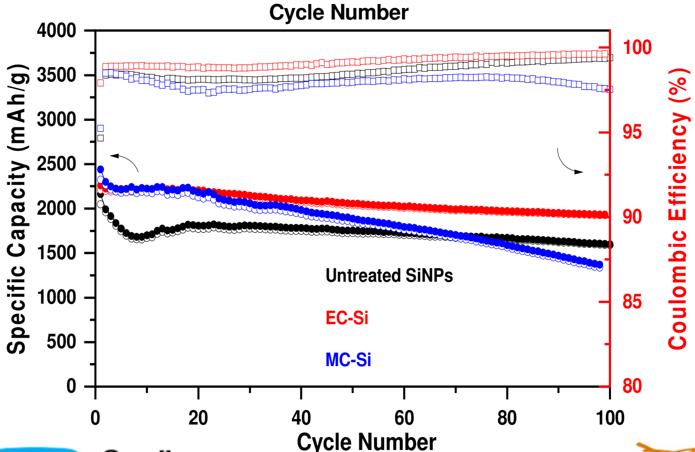


- ❑ Cyclic carbonate group was attached onto the surface of SiNPs *via* Pt(dvs)-catalyzed hydrosilylation reaction.
- ❑ Si nanocrystal structure was well maintained after functionalization.
- ❑ HRTEM, FT-IR, TGA and XPS analysis confirmed the attachment of the organic monolayer on the surface of SiNPs.

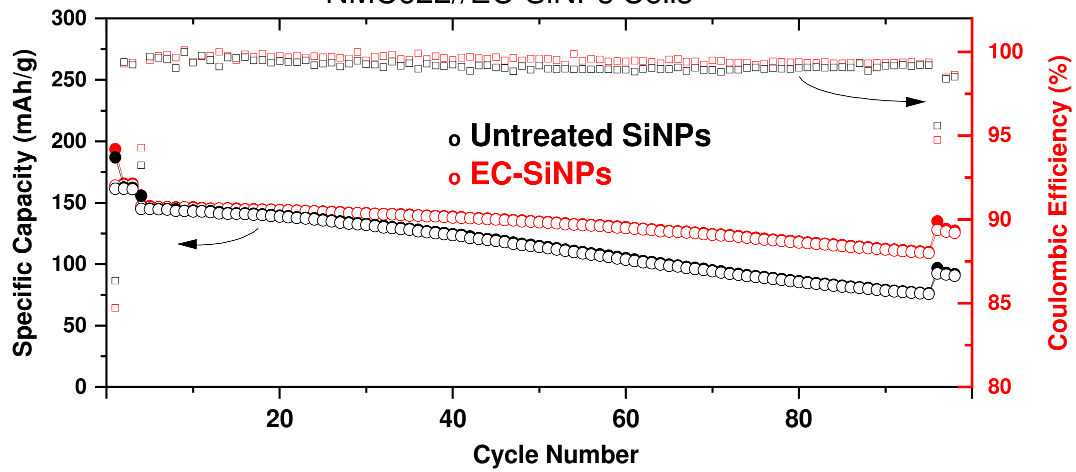
Electrochemical Performance of Cyclic Carbonate-Functionalized SiNPs

3 formation cycle: Si/Li Cell



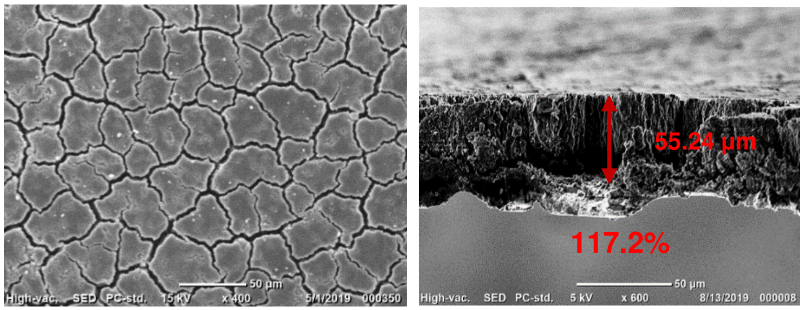


NMC622//EC-SiNPs Cells

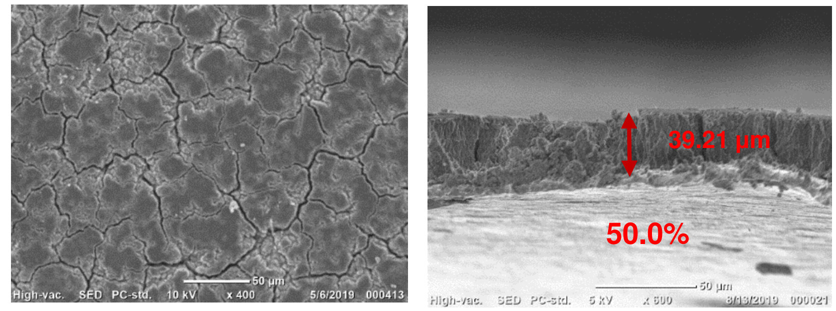


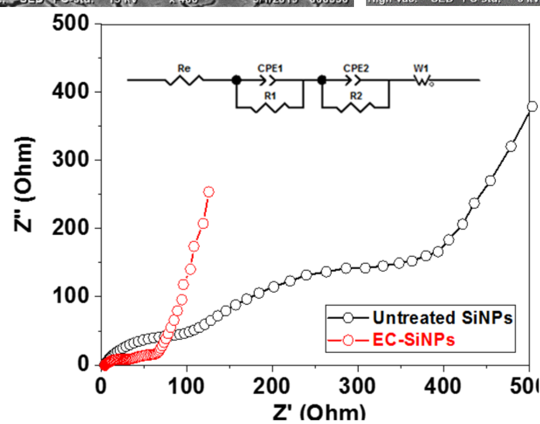
- ❑ EC-SiNPs showed much higher 1st cycle and overall Coulombic efficiency and high capacity compared with the untreated pristine Si anode.
- ❑ NMC622/EC-SiNPs full cell showed improved capacity retention (78% vs 58%) compared with the untreated SiNP anode cell.
- ❑ However, MC-SiNPs with other carbonate surface groups (*i.e.* linear methyl carbonates) showed similar initial capacity but faded rapidly with cycling.

Untreated SiNPs anode after cycling

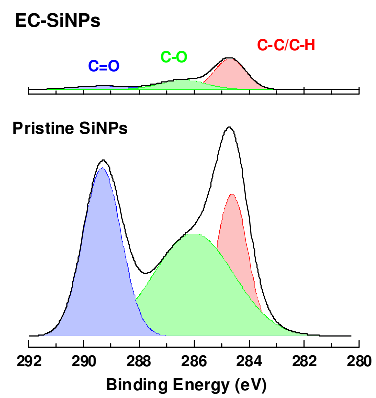


Functionalized EC-SiNPs anode after cycling

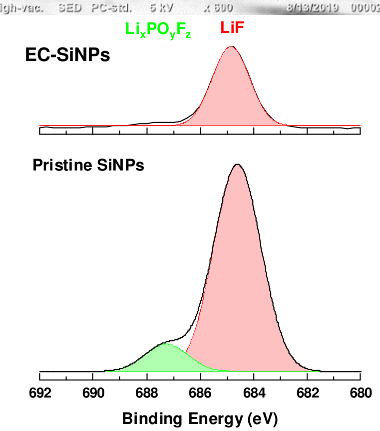




C_{1s} XPS



F_{1s} XPS

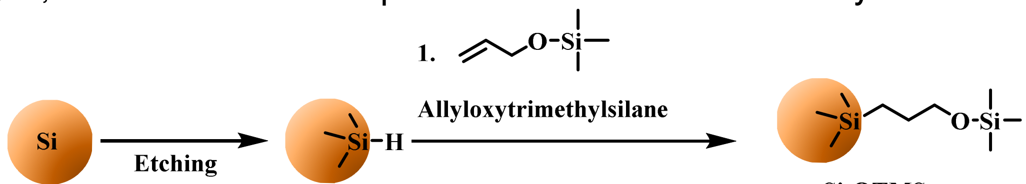


- Surface EC group decomposed *via* a two-electron reduction forming a SEI comprising organic polyolefin inner layer and LiF/covalent bonded LiEDC out layer.
- The unique SEI suppress the side reactions of electrolyte, accommodates the volume expansion and prevents the surface growth and impedance buildup.
- After cycling, the surface cracks and thickness growth for EC-SiNPs anode are reduced owing to the stabilized SEI.

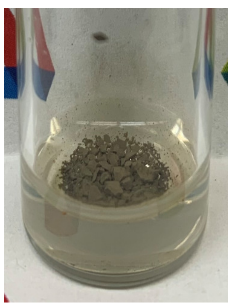
TECHNICAL ACCOMPLISHMENTS AND PROGRESS

(2) SiNPs Surface Functionalization: Non-Polar Silane Surface Group

Design concept: Hydrophobic group on the surface of SiNPs prevents the intimate contact with the hydrophilic electrolyte, thus eliminates the parasitic reactions of electrolyte and the growth of SEI.

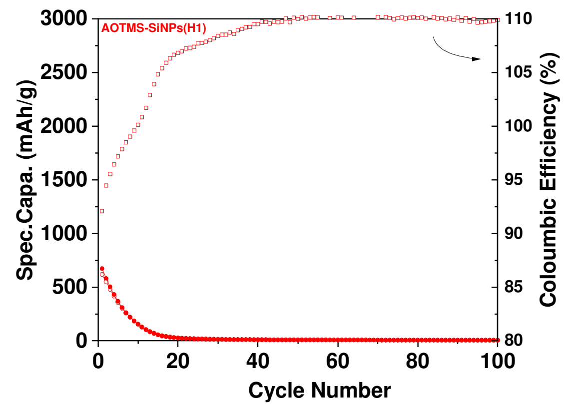


Si-OTMS



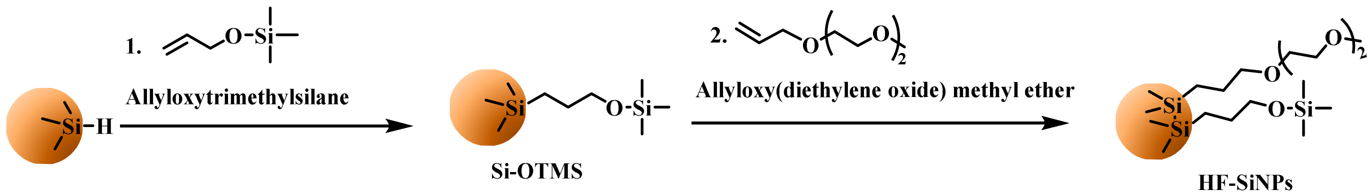
Not dispersible in PAA/H_2O

Li/Si half-cell
70% Si, 20%PAA,10% C45
3 C/20 formation cycles, 100 C/3 cycles
1.5-0.01 V



- SiNPs (Alfa Aesar) with surface trimethylsilane group $-Si(CH_3)_3$ were synthesized *via* hydrosilylation reaction between allyloxy trimethylsilane and Si-H terminated SiNPs synthesized by HF-acid etching.
- Non-polar silane functionalized SiNPs showed little capacity and rapid capacity decay due to the lack of Li^+ conducting channel.

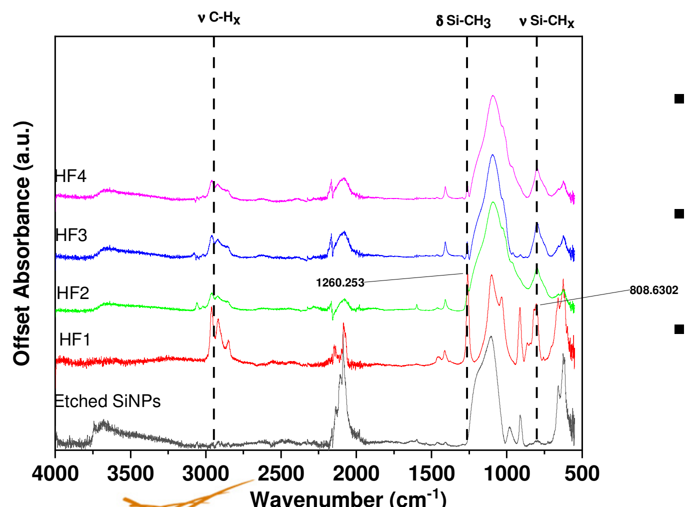
Surface Functionalized SiNPs with a Li⁺ Conducting Channel



A combination of hydrophobic groups and Li⁺ conducting channel

- The 2nd surface group – oligo(ethylene glycol) – provides a conducting channel which only allows Li⁺ go through the surface.
- Oligo(ethylene glycol) group also improves the processability of SiNPs-based anode slurries.

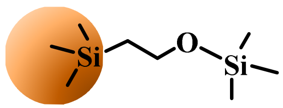
Sample	ATOMS	AEO2M
HF1	1	0
HF-2	1	0.5
HF-3	1	1
HF-4	1	2



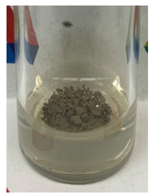
- C-H stretching (~2900 cm^{-1}), Si-CH_3 bending (1260 cm^{-1}) and Si-C stretching (~800 cm^{-1}) peaks appeared.
- Si-O-Si stretching peak (~1100 cm^{-1}) splits due to the introduction of C-O bond on the SiNPs surface.
- C-H stretching (~2900 cm^{-1}) and C-O stretching (~1100 cm^{-1}) peaks become broad due to the introduction of the oligo(ethylene oxide) group.

Electrochemical Performance of Hybrid Functionalized SiNPs

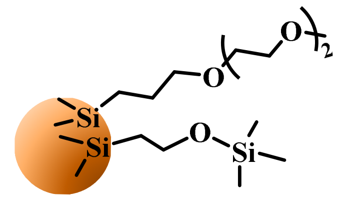
HF-1



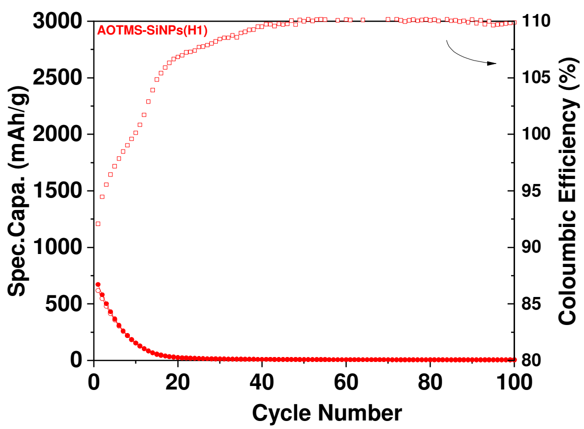
Hydrophobic SiNPs



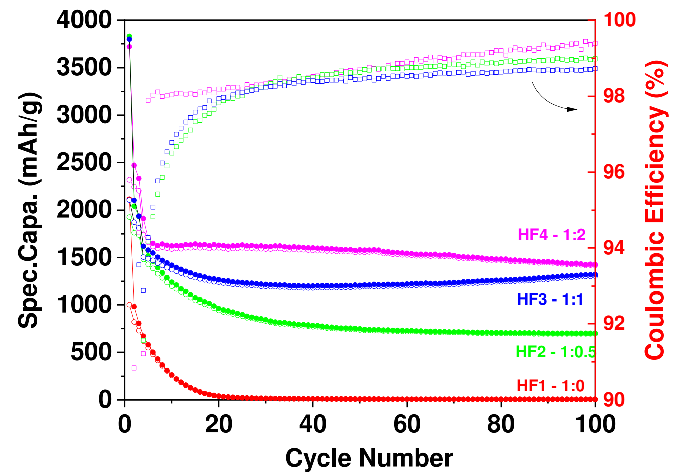
HF-4



Mixed substituted SiNPS



Li/Si half-cell
70% Si,20%PAA,10%C45
3 C/20 formation cycles, 100 C/3 cycles
1.5-0.01 V



- Hybrid functionalized SiNPs can be well dispersed in PAA/H_2O slurry.
- Hybrid functionalized SiNPs significantly improved the initial capacity and capacity retention for Si/Li cell.
- Electrochemical performance improves with increasing substitution ratio of oligoether/silane; HF4-SiNPs with1:2 ratio showed the optimal cell performance.

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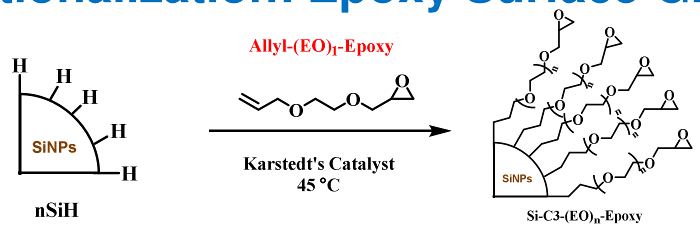
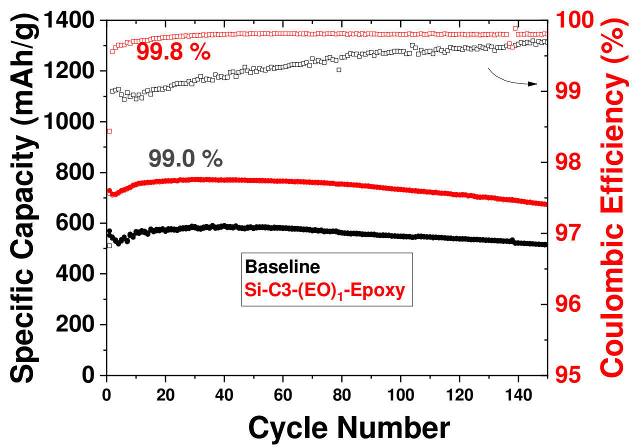
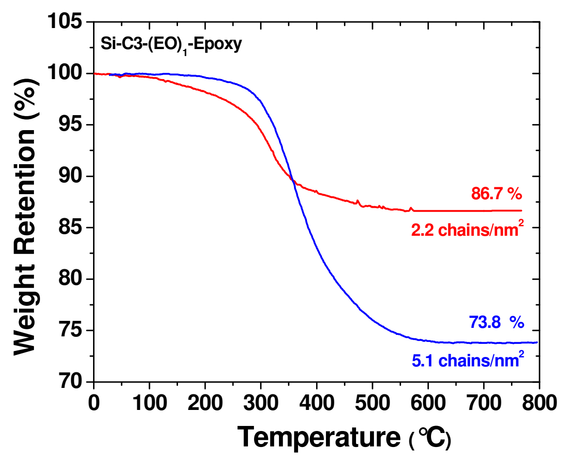
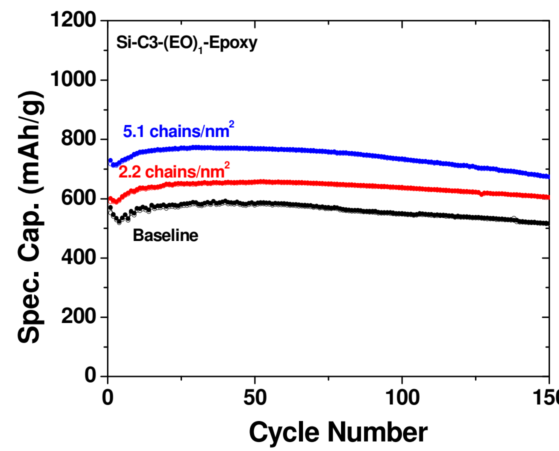
(3) SiNPs Surface Functionalization: Epoxy Surface Group



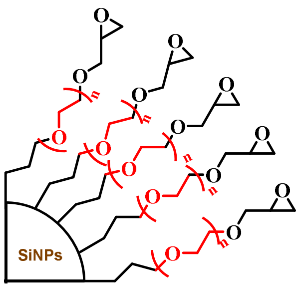




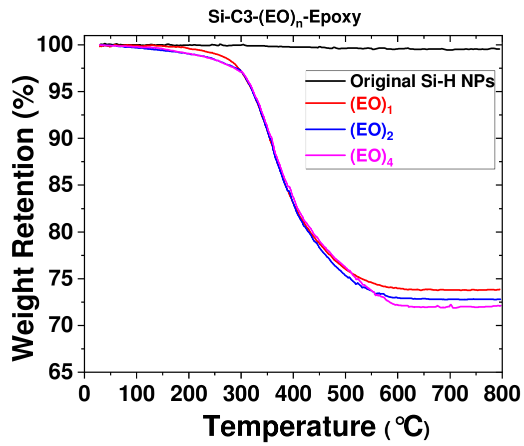


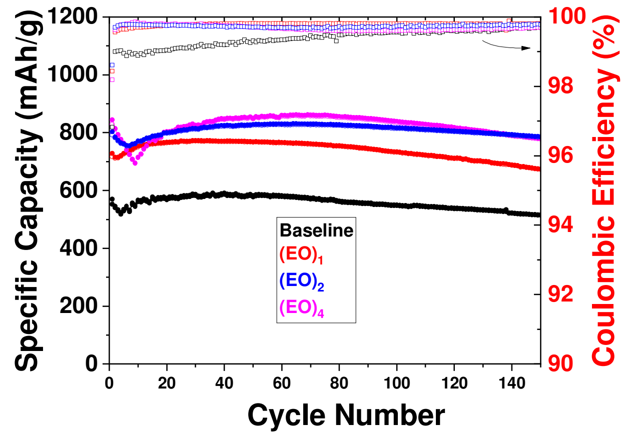
- Epoxy surface group was successfully attached to the surface of SiNPS *via* hydrosilylation reaction.
- The introduction of epoxy surface mitigates the reactivity of the Si anode and improves cycling performance.
- The epoxy group grating density (*surface group/nm²* of SiNPs) impacts the electrochemical performance. The higher the grafting density, the better the cell performance.

Impact of Oligo(ethylene glycol) Chain Length



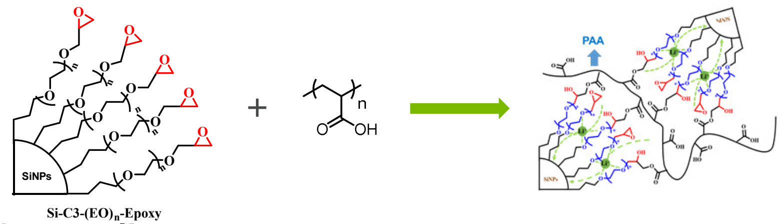
Sample	σ (chains /nm²)
$(EO)_1$	5.1
$(EO)_2$	4.2
$(EO)_4$	3.6

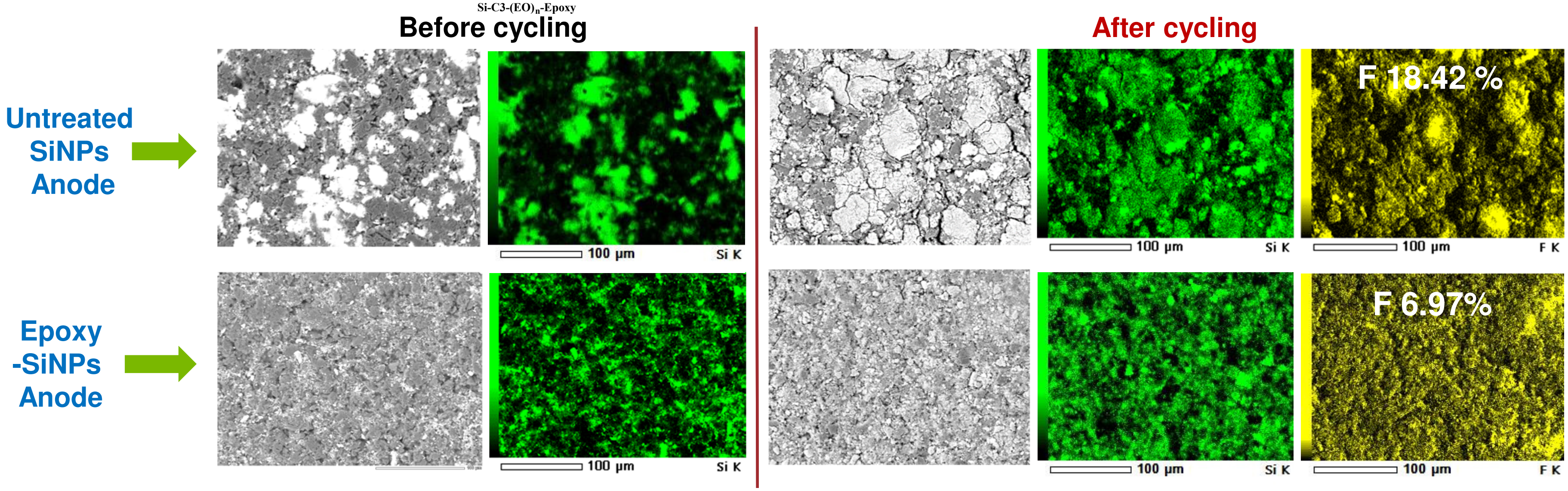




- SiNPs with epoxy surface group comprising different chain length of oligo(ethylene glycol) were synthesized.
- The longer the oligo(ethylene glycol) chain, the lower the grating density.
- Si-C3-$(EO)_4$-epoxy SiNPs have the longest chain but the lowest GD of 3.6 chain/nm^2. This is likely due to the steric hindrance of the longer oligo(ethylene glycol) chain leading to partial hydrosilylation.
- Si-C3-$(EO)_2$-epoxy SiNPs shows the best cell performance due to the combined effect of grafting density and the ideal EO chain geometry, yielding a facile Li^+ coordination and thus facilitating Li^+ transport at the Si/electrolyte interface.

SiNPs Surface Functionalization: Particle-Binder Interaction

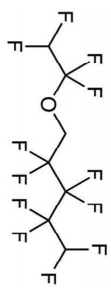




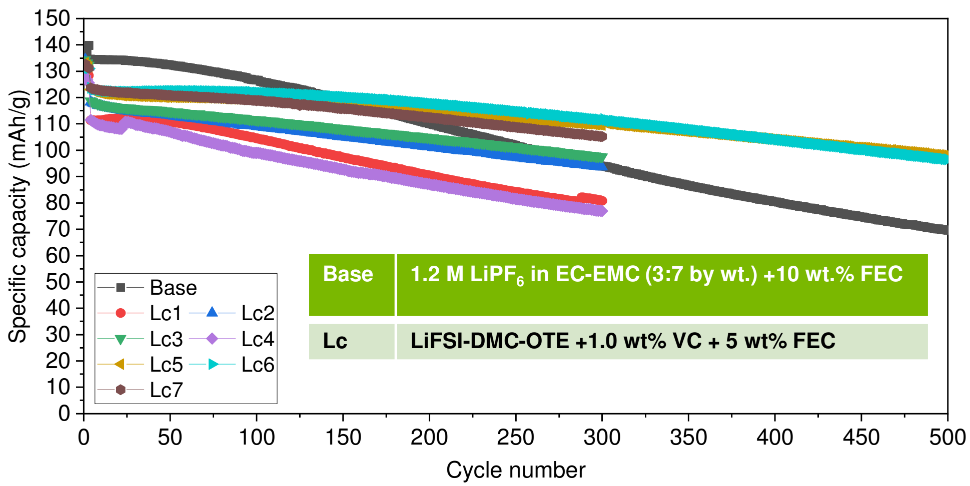
- ❑ Epoxy surface group reacts with the carboxylic acid on the PAA binder *via* a ring-opening reaction forming a covalent bond between the Si nano-particles and the polymer binder.
- ❑ The formation of covalent bond promotes the adherence of Si particles thus enhances the electrode integrity.

(4) New Electrolyte for Interface Stabilization: LHCEs

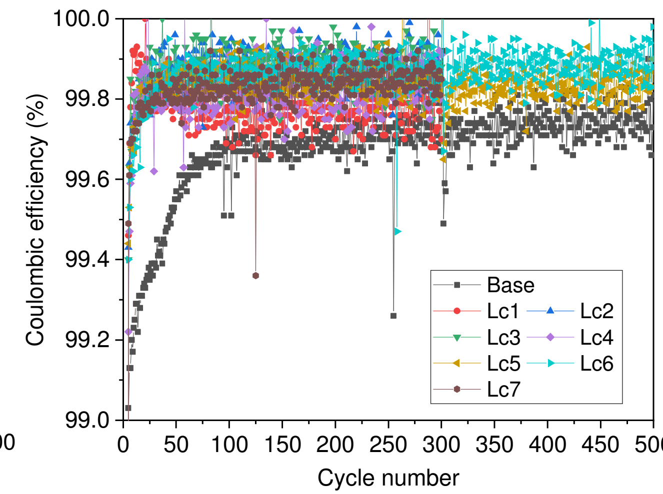
LiFSI-based localized high concentration electrolytes (**LHCEs**) with optimized LiFSI concentration, ratio of diluent and solvent has been developed for Si anodes. With CAMP NMC532 cathodes || BTR1000 (commercial Si-graphite composite) anodes cells, the ***1.8M LiFSI/DMC-OTE (1:2)*** system demonstrated superior long-term cycling performance with the capacity retention of ~***80% after 500 cycles***.



OTE



Base	1.2 M $LiPF_6$ in EC-EMC (3:7 by wt.) +10 wt.% FEC
Lc	LiFSI-DMC-OTE +1.0 wt% VC + 5 wt% FEC



a) Cycling performance of NMC532|| Si/Gr (BTR1000) in OTE-based electrolytes with different salt concentrations and diluent-to-solvent ratios; b) Coulombic efficiency data.

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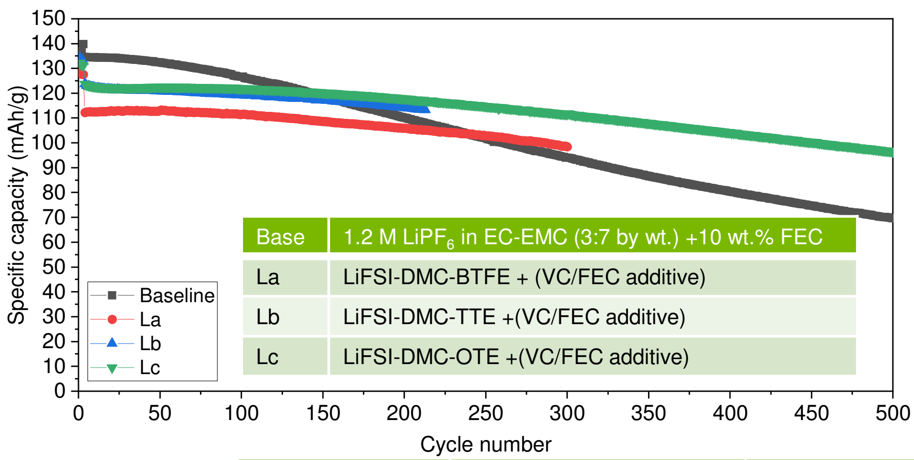
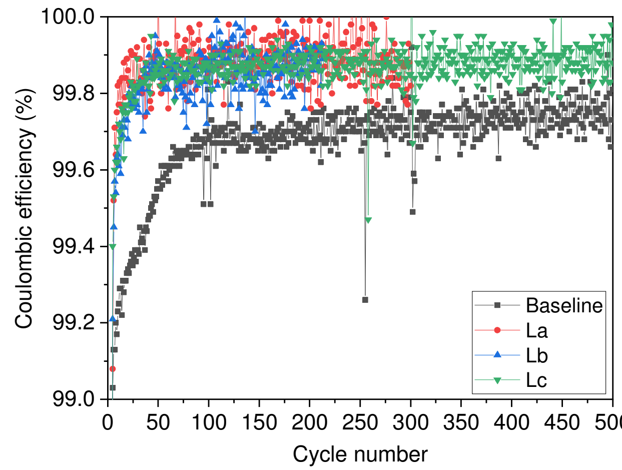
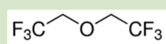
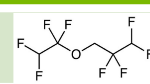
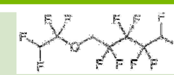
Effect of Different Fluorinated Ether Diluents on Cell Performance

LHCE with OTE diluent and optimized recipe enables NMC532||Si BTR1000 cells with ~80% capacity retention over 500 cycles.



Base	1.2 M $LiPF_6$ in EC-EMC (3:7 by wt.) +10 wt.% FEC
La	LiFSI-DMC-BTFE + (VC/FEC additive)
Lb	LiFSI-DMC-TTE +(VC/FEC additive)
Lc	LiFSI-DMC-OTE +(VC/FEC additive)



	BTFE	TTE	OTE
			
M.W.	182.06	232.07	332.09
B.P. (°C)	62-63	93.2	133
Density (g/ml)	1.404	1.5323	1.654

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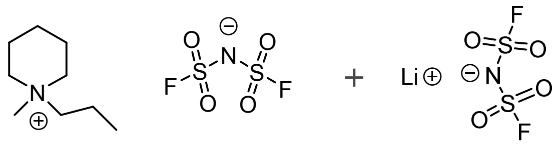
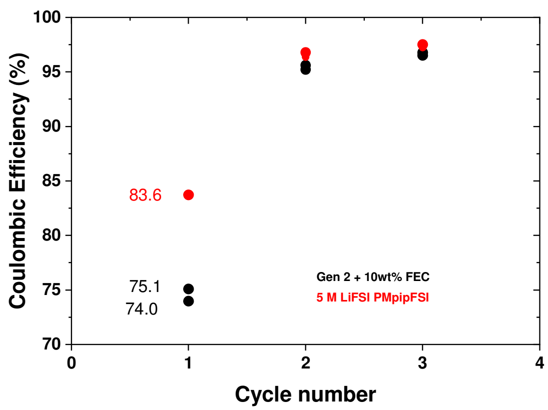
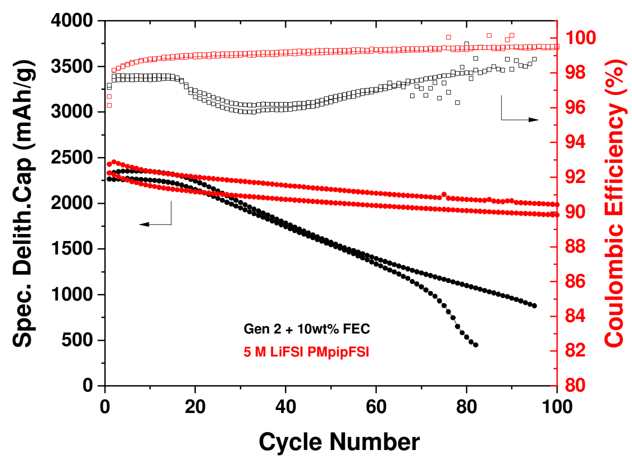
Cycling performance of NMC532|| Si/Gr (BTR1000) in electrolytes with different diluents and Coulombic efficiency data.

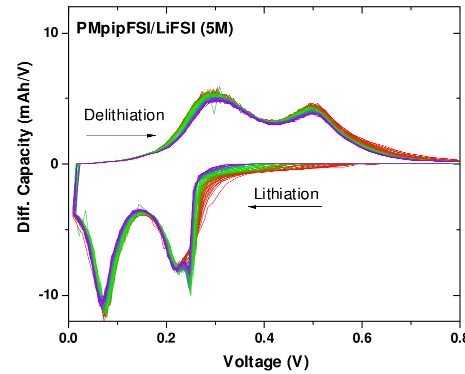
(4) New Electrolyte for Interface Stabilization: FSI-Based Ionic Liquids

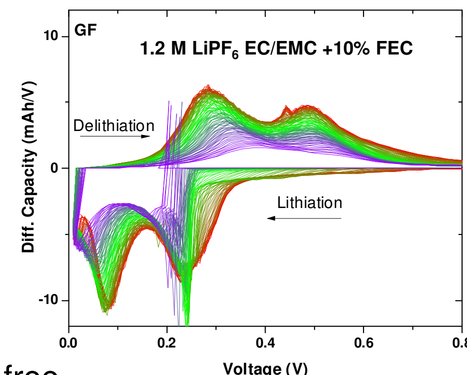


PMpipFSI-LiFSI









- ❑ Ionic liquids are synthesized by a one-step reaction with high yield and purity and halide free.
- ❑ No HF-generation and immune to moisture due to the use of non-hydrolysable FSI^- anions and LiFSI salt.
- ❑ PMpipFSI-LiFSI electrolyte showed 83.6% 1st Coulombic efficiency and much improved cycling performance than Gen 2 +10% FEC with no over-potential buildup owing to the stabilized interface.

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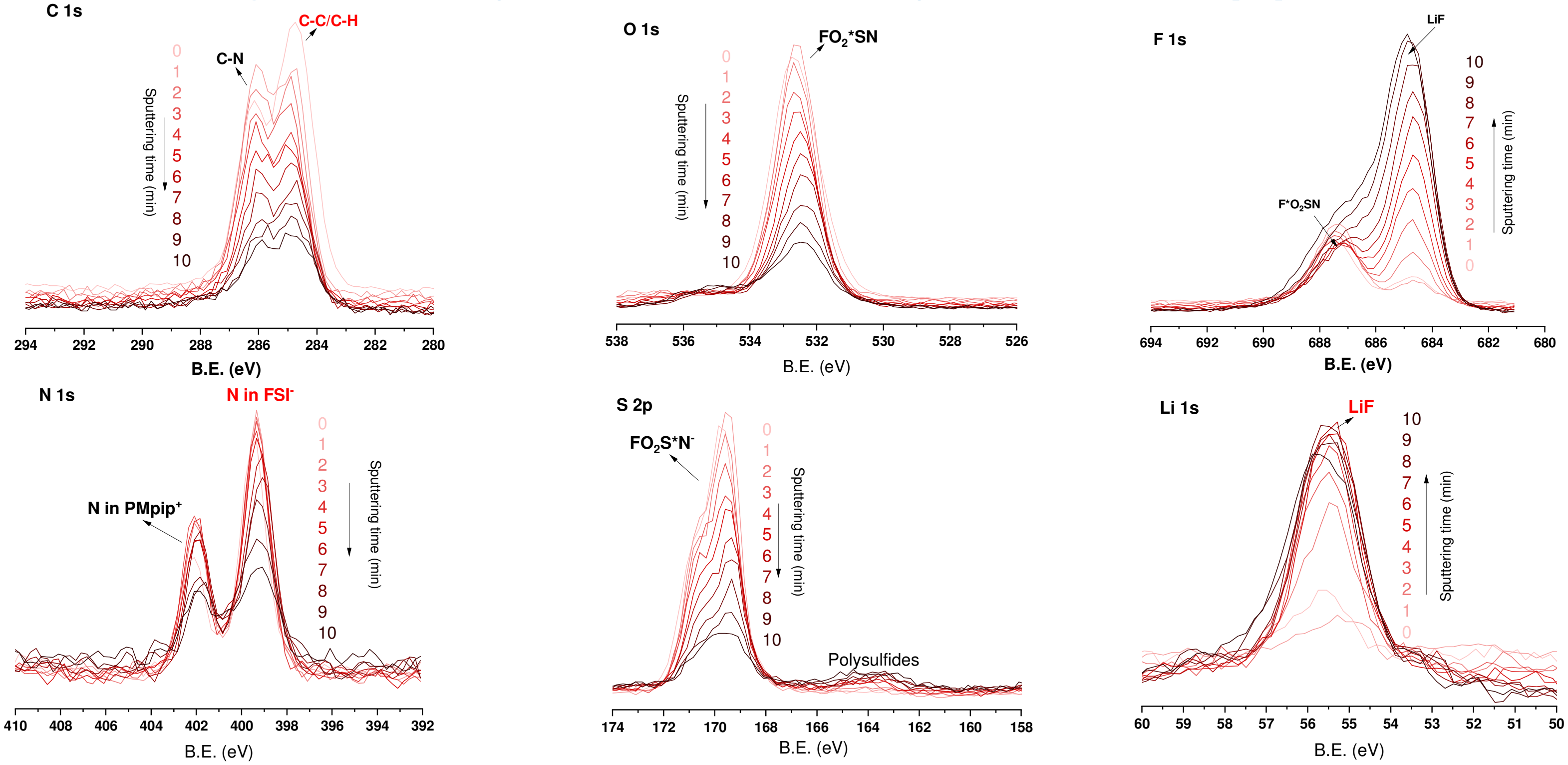
Depth-Profiling XPS Analysis of Si Anode Cycled with PMpipFSI/LiFSI (5M)



- ❑ Ar^+ sputtering started at a one-minute interval to obtain a total of ten XPS spectra at different depths.
- ❑ As sputtering depth increases, the organic species reduces while inorganic species (mainly LiF) gradually increases.
- ❑ Different from the SEI formed by Gen2 +10% FEC, the chemical composition for PMpipFSI/LiFSI formed SEI is consistent at every depth of the surface.

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Six DOE labs have teamed to form this integrated effort focused on gaining insights into and advancement of silicon-based materials, electrode processing, and cells.
- Five DOE core facilities - Battery Abuse Testing Laboratory (BATLab), Battery Manufacturing Facility (BMF), Cell Analysis, Modeling, and Prototyping (CAMP), Materials Engineering Research Facility (MERF), Post-Test Facility (PTF) support this effort.
- This effort has strong interactions within the Si Deep Dive Program (BAT388, BAT439 and BAT440).
- This effort has strong interactions with the Silicon Electrolyte Interface Stabilization (SEISta) program (BAT436, BAT437 and BAT438).

PROPOSED FUTURE RESEARCH

- Continue engineering Si anode interface by particle surface functionalization.
- Continue developing new electrolytes to improve the interfacial stability of Si anode.
- Continue collaboration with SEISta team and work to incorporate their insights into the new material design and development.
- Scale up and validate the performance of surface functionalized SiNPs and electrolytes that showed promising results.

Continue studying the interplay of modified surfaces, electrolyte, laminate properties, and electrochemical cycling performance as a route to improve our understanding of silicon-based electrodes

SUMMARY

Collaborative multi-lab research was performed on functionalized SiNPs materials to improve the interfacial stability that controls the performance of the Silicon-based materials and electrodes.

- ❑ Methods to attach various organic functional groups to the surface of SiNPs *via a* platinum-catalyzed hydrosilylation reaction between –Si-H from the etched SiNPs and allyl terminated functional groups were developed.
- ❑ Organic monolayers were successfully attached and confirmed by FT-IR, XPS, TGA and HRTEM.
- ❑ SiNPs with organic monolayer facilitates the dispersity in aqueous PAA-based slurry making process and homogeneous distribution in the graphite.
- ❑ Cyclic ethylene carbonate surface group participates the SEI formation with much improved 1st Coulombic efficiency than the unfunctionalized Si. NMC622/EC-SiNPs full cells improved capacity retention from 58% to 80% owing to the formation of a stabilized interface mainly comprising organic polyolefin inner layer and LiF/covalent bonded LiEDC outer layer.
- ❑ Non-polar surface groups on SiNPs prevent the intimate contact with hydrophilic electrolyte and mitigate the parasitic reactions with electrolyte while the 2nd oligo(ethylene glycol) group provides a Li^+ channel.
- ❑ LHCE comprising fluorinated ether (OTE) diluent significantly improves the full cell performance; FSI-based ionic liquid electrolyte showed exceptional stability on Si surface evidenced by cell performance and XPS depth-profiling analysis.

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